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(54) Keratotic plug remover

(57) A keratotic plug remover composition comprising a polymer compound having a salt forming group is disclosed. The composition according to the invention can effectively remove keratotic plugs in the skin pores, so that the conspicuousness of the skin pores is mitigated and clean and healthy skin pores can be maintained. The composition does not hurt the skin.

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## Description

### BACKGROUND OF THE INVENTION

#### 5 Field of the Invention:

The present invention relates to a keratotic plug remover which excellently removes keratotic plugs formed in the pores of the skin, and a method of removing keratotic plugs from the skin utilizing such a keratotic plug remover.

#### 10 Discussion of the Background:

Having conspicuous pores in the skin is a serious skin problem, especially for women, and is mainly caused by keratotic plugs formed in the pores of the skin. Keratotic plugs are dead epidermal cells keratinized together with sebaceous matters and dirt which plug the pores of the skin. If proper treatment is not given, not only conspicuous pores but also various skin troubles result. Accordingly, removal of keratotic plugs is advisable in view of the health and beauty of the skin.

Ordinary face detergents, make-up removers, however, cannot sufficiently remove the keratotic plugs.

Pack preparations, which are applied to the skin and peeled off after dried, and which generally contain a nonionic polymer such as polyvinyl alcohol and polyvinyl pyrrolidone as a major component of a film forming agent, are still not sufficiently effective for removing dirt from the skin pores and especially for removing keratotic plugs.

Thus, there remains a need for a keratotic plug remover which can effectively remove keratotic plugs formed in the pores of the skin and a method of removing keratotic plugs from the skin utilizing such plug removers.

### SUMMARY OF THE INVENTION

Accordingly, it is one object of the present invention to provide novel keratotic plug removers which effectively remove keratotic plugs from the skin.

It is another object of the present invention to provide a method for removing keratotic plugs from the skin which utilized such keratotic plug removers.

These and other objects which will become apparent during the following detailed description have been achieved by the inventors discovery that a keratotic plug remover which comprises a synthetic polymer having a salt forming group can effectively remove keratotic plugs and dirt from the pores of the skin.

### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The salt forming group of the polymer which is useful in the present invention is not particularly limited as long as it can form a salt in the presence of an acid or a base, and anionic, cationic and amphoteric groups are suitable. Examples of the salt forming group are carboxyl, sulfonic acid group, sulfuric acid residual group ( $-\text{OSO}_3\text{H}$ ), phosphoric acid residual group ( $-\text{OPO}_3\text{H}_2$ ), nitric acid residual group ( $-\text{NO}_2$ ), amino group, ammonium group, and the like. Two or more of these groups may be present in one compound.

The polymer compound which is useful in the present invention is preferably water-soluble from the viewpoint of good appearance, but it is not necessarily water-soluble for the purpose of achieving the effects of this invention. The compounds which are not water-soluble may take the form of dispersion and/or emulsion.

Examples of the polymers useful in the present invention include: hyaluronic acid, sodium hyaluronate, sodium chondroitin sulfate which are mucopolysaccharides; alginic acid, sodium alginate, ammonia alginate, sodium carboxymethylcellulose, and carboxymethyl amylose which are hemicelluloses. These are of natural origin or semi-synthesized polymers. In this invention, synthesized polymers are more preferable. Examples of the synthesized polymers include (A) polymers of one or more monomers listed in (1) to (3) below, (B) copolymers of the monomers as listed in (1) to (3) and another monomer which has no salt forming group, such as vinyl esters of aliphatic carboxylic acid such as vinyl acetate, (meth)acrylic esters such as ethyl methacrylate, alkyl vinyl ethers such as methyl vinyl ether, N-vinyl cyclic amides such as N-vinylpyrrolidone, styrene and alkyl-substituted styrene, and (C) mixtures of the above-mentioned polymers.

#### (1) Anionic monomers:

Acrylic acid (AA), Methacrylic acid (MA), Maleic acid, itaconic acid and the like, which are unsaturated carboxylic acid monomers or their anhydrides or their salts;  
Styrene sulfonic acid, 2-Acrylamide-2-methyl propane sulfonic acid (AMPS) and the like, which are unsaturated sulfonic acid monomers or their salts;

of the composition.

Example 1:

Keratotic plug removers were prepared according to the pack preparation method mentioned below using the polymers listed in Table 1. A panel washed their face and used the preparation on their faces at an application rate of 0.1 ml/cm<sup>2</sup>. The conditions of use were a temperature of 25°C, 50% humidity for 30 minutes. When 30 minutes had passed, the pack was peeled off. The ratio of removal of the keratotic plugs was calculated according to the following equation for evaluation.

$$\text{Removal ratio of keratotic plugs} = \frac{\text{number of keratotic plugs adhered on } 1\text{ cm}^2 \text{ pack}}{\text{number of keratotic plugs existing in the } 1\text{ cm}^2 \text{ wing skin of nose}} \times 100$$

The results are also shown in Table 1.

Evaluation:

- A: over 20% removal ratio of keratotic plugs
- B: 5 to 20% removal ratio of keratotic plugs
- C: less than 5% removal ratio of keratotic plugs

Preparation:

Polymer	15 to 20% by weight
Glycerol	5
HCO60 (polyoxyethylene hydrogenated castor oil 60EO adduct)	1
Ethanol	5
Perfume	0.5
Antiseptic	suitable amount
Purified water	67.5 to 72.5
Total	100.0

Table 1

IONIC	Polymers	Anionic/ Cationic	Evaluation (Removal of keratotic plugs)
IONIC	Poly 2-acrylamido-2-methylpropane sulfonate (AMPS) (MW: 500,000)	Anionic	A
	Polymethacryloyloxymethyl succinate (MW: 200,000)	Anionic	A
	Polymer of Na-styrene sulfonic acid (NaSS) (MW: 100,000)	Anionic	A
	Polymer of methacrylic acid (MAA) (MW: 200,000)	Anionic	A
	Copolymer of NaSS/MAA (1:1) (MW: 400,000)	Anionic	A
	Polymethacryloyloxyethyl trimethyl ammonium chloride (QDM) (MW: 400,000)	Cationic	A
	Polymethacryloyloxyethyl triethyl ammonium diethyl sulfate (DEMA-DES) (MW: 300,000)	Cationic	A
	Polymethacrylamidepropyl trimethyl ammonium chloride (MAPTAC)/polyacrylamidepropyl trimethyl ammonium chloride (DMA/AM-Q) copolymer (8:2 by molar ratio) (MW: 300,000)	Cationic	A
NONIONIC	Polyvinyl alcohol (PVA) (MW: 100,000)	-	C
	Polyethylene oxide (PEO) (MW: 1,000,000)	-	C
	Fullulan (MW: 70,000)	-	C
	Hydroxyethylcellulose (HEC) (MW: 100,000)	-	C
	Polyvinyl pyrrolidone (PVP) (MW: 600,000)	-	C

Keratotic plug removers were prepared using the polymers listed in Table 2, and the removal ratio of keratotic plugs and the pain at the time of peeling-off were checked.

5 The polymers were individually prepared into an aqueous 20-30% by weight solution, and members of the panel used in the same manner as in Example 1.

Removals ratio of keratotic-plugs:

10 See the equation in Example 1.

Evaluation:

(Removal ratio of keratotic plugs)

15

A: 35% or more

B: 20 to 34%

C: 5 to 19%

D: less than 5%

20

(Pain at the time of peeling-off)

slight pain: +

considerable pain: ++

25

30

35

40

45

50

55

Table 2

Polymers	Anionic/ Cationic	Removal of Keratotic plugs	Pain upon peeling-off
Poly-2-acrylamide-2-methylpropane sulfonate (AMPS) (MW: 500,000)	Anionic	D	++
Polymethacryloyloxymethyl succinate (MW: 200,000)	Anionic	B	+
Polymer of Na-styrene sulfonic acid (NaSS) (MW: 100,000)	Anionic	A	++
Methacrylic acid (MAA) polymer (MW: 200,000)	Anionic	B	++
NaSS/MAA copolymer (1:1) (MW: 400,000)	Anionic	A	++
Polymethacryloyloxyethyl trimethylammonium chloride (QDH) (MW: 400,000)	Cationic	A	+
Polymethacrylamidepropyl trimethylammonium chloride (MAPTAC) (MW: 300,000)	Cationic	A	+
MAPTAC/polyacrylamidepropyl trimethyl ammonium chloride (DMAPAAm-Q) copolymer (8:2) (MW:300,000)	Cationic	A	+
MAPTAC (MW: 300,000)/QDH (MW: 400,000) mixture	Cationic	A	+

Keratotic plug removers having the formulations as in Table 3 were prepared according to the conventional manner, and the keratotic plug removing performance was evaluated. The results are shown in Table 4.

#### Evaluation method:

Panel members washed their faces and applied keratotic plug removers onto their cheeks (0.1 ml/cm<sup>2</sup>). The application was allowed to set at 25°C, humidity 50% for 30 minutes, and subsequently the pack film was peeled off. The number of the members who used an invention product A on their left cheek and an invention product B on their right cheek was the same as the number of the members who used an invention product B on their left cheek and an invention product A on their right cheek.

The panel members evaluated the removers by answering "Invention product A removed better", "Invention product A and Invention product B were almost the same concerning the removal performance" or "Invention product B removed better", and their percentages were obtained.

Table 3

Components (% by weight)	Invention products A			Invention products B	
	1	2	3	1	2
Poly-2-acrylamide-2-methylpropane sulfonate (AMPS) (MW: 500,000)	25	25	-	25	-
Polymethacryloyloxyethyltrimethyl ammonium chloride (QDM) (MW: 400,000)	-	-	25	3	25
Silica (av. particle size = 5 micrometers)	-	-	10	-	-
Zinc oxide (av. particle size: 0.04 micrometers)	3	-	-	-	-
Sericite (long axis: 5 to 10 micrometers)	-	10	-	-	-
HCO40 (Polyoxyethylene hydrogenated castor oil 40 EO adduct)	3	3	3	3	3
Glycerol	5	5	5	5	5
Perfume	0.5	0.5	0.5	0.5	0.5
Antiseptic	suitable amount				
Purified water	balance				

Table 4

Left (Right) - Right (Left)	Invention product A removed better	Invention products A and B are similar	Invention product B removed better
Invention product A1 -Invention product B1	90	10	0
Invention product A2 -Invention product B1	90	10	0
Invention product A3 -Invention product B2	80	20	0

#### Example 4:

The keratotic plug removers as formulated in Table 5 were prepared according to the conventional manner.

The obtained keratotic plug removers were used by a panel consisting of 20 members as in the same manner described in Example 1. The pain upon peeling-off was evaluated with the criteria below. The results are shown in Table 5. Concerning the keratotic plug removal, all preparations removed well.

5 Evaluation:

O: No pain felt  
X: Pain felt

Table 5

Components (% by weight)	Invention products C			Invention products D	
	1	2	3	1	2
Poly-2-acrylamide-2-methylpropane sulfonate (AMPS) (MW: 500,000)	25	25	-	25	-
Polymethacryloyloxyethyl triammonium chloride (QDM) (MW: 400,000)	-	-	25	-	25
Tri-2-ethyl hexanoic glycerol	3	-	3	-	-
2-Ethylhexanoic diglyceride	-	3	-	-	-
Glycerol	5	5	5	5	5
HCO40 (Polyoxyethylene hydrogenated castor oil 40 EO adduct)	1	1	1	-	1
Squalane	1	1	1	-	-
Ethanol	5	5	5	5	5
Perfume	0.5	0.5	0.5	0.5	0.5
Antiseptic	suitable amount				
Purified water	balance				
Pain when peeled off	O	O	O	X	X

Example 5:

The keratotic plug removers as formulated in Table 6 were prepared according to the conventional manner. The obtained keratotic plug removers removed keratotic plugs effectively without giving pains at the time of peeling off.



Table 6

Components (% by weight)	Invention products E									
	4	5	6	7	8	9	10	11	12	13
Polymethacrylamidepropyl trimethylammonium chloride (MAPTAC) (MW: 500,000)									10	10
Polymethacryloyloxyethyl trimethylammonium chloride (QDM) (MW: 400,000)							10	10		
Na • Styrene sulfonic acid / Methacrylic acid copolymer (MW: 400,000)	25									
Poly 2-acrylamide-2-methylpropane sulfonate (AMPS) (MW: 500,000)		30				20				
Polymethacrylamidepropyl trimethylammonium chloride (MAPTAC) (MW: 50,000)			35					20		20
Polymethacryloyloxyethyl trimethylammonium chloride (QCM) (MW: 70,000)				30	20		20		20	
Polyvinyl alcohol (MW: 30,000)										
PEG 200 (polyethylene glycol 200)	5	5	5	5	5	5				
HCO 40 (Polyoxyethylene hydrogenated castor oil 40 EO adduct)	1	1	1	1	3	3	3	3	3	3
Squalane					1	1	1	1	1	1
2-ethylhexanoic diglyceride	1	1	1	1	1	1	1	1	1	1
Tri-2-ethylhexanoic glycerol	3				2		3	3	3	3
1-Hexyl-3-undecamethylhexasiloxane propynyl glycerol	1	2								
1-isostearoyl-3-myristoylglycerol				3		2		2		2
Silica		2	3				3			
Sericite				10					3	
Perfume			10							
Antiseptic	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Water										

← suitable amount →

← balance →

## Example 6:

A keratotic plug remover having the following formulation was prepared.

Polymethacryloyloxy trimethylammonium chloride (QDM) (MW: 400,000)	27.0 wt. %
Sorbitol	3.0
Sericite	3.0
Ethanol	5.0
Antiseptic	suitable amount
Water	balance

Example 7:

A keratotic plug remover having the following formulation was prepared.

Polymethacryloyloxy trimethylammonium chloride (QDM) (MW: 250,000)	27.0 wt. %
Polyoxethylene hydrogenated castor oil (E.O. 20)	2.0
Squalane	0.5
1-Isostearoyl-3-myristoyl glycerol (DGMI)	1.5
86% Glycerol	2.0
Propylene glycol	1.0
Sericite	3.0
Ethanol	5.0
Antiseptic	suitable amount
Water	balance

Example 8:

A keratotic plug remover having the following formulation was prepared.

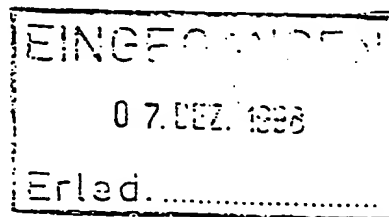
Polymethacryloyloxy trimethylammonium chloride (QDM) (MW: 200,000)	15.0 wt. %
Polymethacrylamidepropyl trimethyl ammonium chloride (MAPTAC) (MW: 300,000)	15.0
Polyoxyethylene hydrogenated castor oil (E.O. 40)	1.5
Squalane	0.5
2-Ethylhexanoic triglyceride	2.0
Sorbitol	3.0
Kaolin	7.0
Titanium oxide	2.0
Ethanol	5.0
Antiseptic	suitable amount
Water	balance

Claims

1. Use of a composition, comprising a polymer compound having a salt forming group, as a keratotic plug remover.
2. The use as claimed in Claim 1, wherein said polymer compound is a synthetic polymer.
3. The use as claimed in Claim 1, wherein said salt forming group is selected from the group consisting of a carboxyl group, sulfonic acid group, sulfuric acid residual group, phosphoric acid residual group, nitric acid residual group, amino group and an ammonium group.
4. The use as claimed in Claim 1, wherein said polymer compound having a salt forming group has a molecular weight of from 10,000 to 1,500,000.
5. The use as claimed in Claim 1, wherein the amount of said polymer compound having a salt forming group is 0.01 to 70% by weight based on the total weight of said composition.

6. Use of a composition, comprising a polymer compound having a salt forming group and a solvent, as a keratotic plug remover.
7. The use as claimed in Claim 6, wherein the amount of said polymer compound having a salt forming group is 0.01 to 70% by weight, and the amount of said solvent is 30 to 99.99% by weight based on the total weight of said composition.
8. Use of a composition, comprising a polymer compound having a salt forming group and a pigment, as a keratotic plug remover.
9. The use as claimed in Claim 8, wherein the amount of said polymer compound having a salt forming group is 0.01 to 70% by weight, and the amount of said pigment is 0.1 to 70% by weight based on the total weight of said composition.
10. Use of a composition, comprising a polymer compound having a salt forming group, a pigment and a solvent, as a keratotic plug remover.
11. The use as claimed in Claim 10, wherein the amount of said polymer compound having a salt forming group is 0.01 to 70% by weight, the amount of said pigment is 0.1 to 70% by weight and the amount of said solvent is 29.99 to 99.99% by weight based on the total weight of said composition.
12. Use of a composition, comprising a polymer compound having a salt forming group and an oil component, as a keratotic plug remover.
13. The use as claimed in Claim 12, wherein the amount of said polymer compound having a salt forming group is 0.01 to 70% by weight and the amount of said oil component is 0.01 to 30% by weight, based on the total weight of said composition.
14. Use of a composition, comprising a polymer compound having a salt forming group, an oil component and a solvent, as a keratotic plug remover.
15. The use as claimed in Claim 14, wherein the amount of said polymer compound having a salt forming group is 0.01 to 70% by weight, the amount of said oil components is 0.01 to 30% by weight and the amount of said solvent is 29.99 to 99.98% by weight based on the total weight of said composition.
16. Use of a composition, comprising a polymer compound having a salt forming group, a pigment and oil component, as a keratotic plug remover.
17. Use of a composition, comprising a polymer compound having a salt forming group, a pigment, an oil component and a solvent, as a keratotic plug remover.
18. A method for removing keratotic plugs which comprises applying a keratotic remover composition as claimed in Claims 1, 6, 8, 10, 12, 14, 16 or 17 onto the skin, and peeling off after the composition is dried.

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Anmelder/Applicant/Demandeur/Patentinhaber/Proprietor/Titulaire KAO CORPORATION	

## COMMUNICATION

The European Patent Office herewith transmits as an enclosure the European search report for the above-mentioned European patent application.

If applicable, copies of the documents cited in the European search report are attached.

☒ Additional set(s) of copies of the documents cited in the European search report is (are) enclosed as well.

The following specifications given by the applicant have been approved by the Search Division:

☒ abstract

☒ title

☐ The abstract was modified by the Search Division and the definitive text is attached to this communication.

The following figure will be published together with the abstract: NONE

## REFUND OF THE SEARCH FEE

If applicable under Article 10 Rules relating to fees, a separate communication from the Receiving Section on the refund of the search fee will be sent later.





## DOCUMENTS CONSIDERED TO BE RELEVANT

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Place of search THE HAGUE		Date of completion of the search 4 December 1997	Examiner Couckuyt, P
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X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			



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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
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